CONVERSION ELECTRON AND X-RAY MÖSSBAUER STUDIES OF THE CORROSION PRODUCTS AND SURFACE MODIFICATIONS IN STAINLESS AND WEATHERING STEELS

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The study of the corrosion products formed on the surface of Type 316 stainless steel exposed to chlorinated seawater for 18 days shows that ferrihydrite and lepidocrocite are the first oxides to form. The surface also shows the formation of a martensite when it is cleaned by light brushing before exposure.

Samples of weathering steel, ASTM A242 Type 1, exposed for 5 1/2 years to either a marine or inland rural environment have been studied between 100K and 400K using CEMS and XMS. Different amounts of hydroxides are present on the surface of each sample. The steel exposed to the inland environment contains more α-FeOOH.

1. INTRODUCTION

A study has been made of the corrosion products formed on the surfaces of stainless and weathering steels which have been subjected to different environmental conditions. The results represent only a small part of the overall study and concentrate on identifying the oxides formed, the relative amounts of each species and their proximity to the steel surface. For each sample, the spectra have been recorded in backscattering geometry using conversion electron (CEMS) or X-ray (XMS) Mössbauer spectroscopy. At room temperature, many oxides, formed as a result of weathering, exhibit similar quadrupole splitting, especially if they are present in the form of fine particles. This makes the identification of each compound difficult. The samples have thus been studied at temperatures between 100K and 400K to help in the identification of these products by use of the temperature-dependent magnetic interaction present in most iron oxides.

2. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Type 316 stainless steel coupons were exposed to chlorinated (1ppm) natural seawater for 18 days. The coupons were suspended vertically in the seawater by a thin nylon cord passed through a 9mm hole punched in the center. Initially, the coupons had been pickled in nitric acid for two minutes and brushed lightly with a nylon brush and detergent. It was subsequently determined that this cleaning procedure was detrimental to the austenitic surface structure, and the exposure was repeated using surfaces which had not been degreased or cleaned in any way. Unexposed stainless steel coupons were used as a standard to monitor the amount of surface structural changes in the exposed coupons. One had been degreased as described above, the other was as received from the mill.

Two samples of weathering steel (ASTM A242 Type 1) were exposed to the atmosphere, one in a marine environment at the Kure Beach, NC 250m test lot for 5.4 years and the other at the inland rural site in Saylorsburg PA, for 5.7 years. All samples were studied between 400K and 100K in a gas flow proportional counter /1/ using a 100mCi

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$^{57}$Co in Rh source. At room temperature, CEMS and XMS spectra were recorded over two different velocity ranges ($\pm 9\text{mm/s}$ and $\pm 3\text{mm/s}$) in order to obtain good resolution in a particular region of interest. The source was kept at room temperature for all experiments.

3. RESULTS

The standard sample of stainless steel which had been cleaned showed visible signs of minor abrasion on the surface. Figure 1a of the room temperature Mossbauer spectrum shows a large amount of martensite was formed and subsequent spectra recorded using the exposed samples which had also been initially cleaned were hard to interpret accurately, even though small amounts of oxide were present. The experiments were repeated using samples which had not been cleaned and Figure 1b shows the spectrum of the unexposed sample. No signs of surface deformation or oxidation are evident on the austenitic structure. The steel exposed to chlorinated seawater showed visible signs of overlapping adherent films which varied in color from orange-grey to orange, to orange-brown which is typical for steel surfaces in an early stage of corrosion. The entire film itself was very granular but not powdery. It could be easily wiped from the surface of the steel. Figures 1c,d show the room temperature CEMS spectra of the region. The sample was then run at 200K without removing it from the detector and the resulting spectra are shown in Figures 1e,f.

The high velocity spectrum of Figure 1c shows that at 300K, no magnetic ordering is present and that oxides present appear to be represented by a quadrupole split doublet superimposed on the stainless steel peak. However inspection of Figure 1d shows that the high velocity peak is not symmetric and that at least two components are present. The low temperature spectra show a small amount of a magnetic splitting present and the high velocity peak is still asymmetric. Fitting of the spectra as well as the difference spectrum obtained after subtracting the standard stainless steel peak, indicates that the major components present are $\gamma$-FeOOH, ferricydrite and a small amount of $\alpha$-FeOOH. Table 1 summarizes the Mossbauer parameters of each oxide. Isomer shifts are relative to $\alpha$-iron. It is evident that the $\alpha$-FeOOH is exhibiting superparamagnetic properties $^{2/7}$.

The samples of weathering steel, although similar in color, did show significant differences in texture when observed through a microscope. Each sample was generally dark brown in color with regions of lighter brown and orange. The corroded layer (estimated to be 50$\mu$m thick) was very adherent to the samples which were also highly pitted as a result of the long exposure. The surface of the sample exposed to the marine environment (Kure Beach NC) was covered in small brown, brittle scaly platelets which when scraped with a metal spatula revealed large amounts of very fine orange-yellow powder below. The surface of the other sample exposed in Saylorsburg PA, was covered with a crust of dark brown nodules protruding from the surface. Most of the nodules were glassy in appearance and scratching the surface again revealed a fine orange-yellow powder underneath.

Some of the spectra obtained from the weathering steel samples are shown in Figure 2. The low velocity CEMS spectra recorded at 400 K (Figures 2a,b) show that different amounts of oxide are present in each sample as indicated by the relative intensities of the two peaks. High velocity spectra recorded between 200K and 400K indicate that a small amount of magnetically ordered $\gamma$-Fe$_2$O$_3$ is present. CEMS spectra recorded at 300K (Figures 2c,d) show indications of superparamagnetic relaxation in one of the compounds identified as $\alpha$-FeOOH. In each case the $\alpha$-FeOOH was fitted with two sextets with broad lines. The sample exposed to the inland environment appears to
contain considerably more $\alpha$-FeOOH, especially in the near surface region probed by the CEMS technique. However XMS of each sample, recorded at 300K (Figures 2g, h) show that considerably more $\alpha$-FeOOH is present below the surface. This difference is attributed to the thickness of the crusty outer material described above. A report of this material, tentatively identified as amorphous ferric hydroxoxide /3/, will soon be published.

At 100K the CEMS spectra in Figures 2g, h show the peaks of $\alpha$-FeOOH as better resolved due to the slowing down of the relaxation rate. The spectra have again been fitted using two sextets. It is apparent from these spectra and others recorded between 300K and 100K that a small field distribution is present at each site in $\alpha$-FeOOH. The quadrupole split doublet present at all temperatures down to 100K is identified as consisting largely of $\gamma$-FeOOH and a small amount of ferrihydrate. A summary of fitted parameters is given in Table 2.

4. CONCLUSION

The cleaning of stainless steel surfaces using abrasive methods is common but does not provide a good standard for samples undergoing studies involving the detection of corrosion rates due to pitting and crevice corrosion. It is well known that martensitic stainless steels are more susceptible to corrosion in seawater. The formation of oxides on stainless steel is appreciable after short
Fig. 2. CEMS and XMS spectra of weathering steel exposed to marine environment at Kure Beach NC or inland rural environment of Saylorsburg PA.
PA (a) CEMS 400K, (c) CEMS 300K, (e) XMS 300K and (g) CEMS 100K.
NC (b) CEMS 400K, (d) CEMS 300K, (f) XMS 300K and (h) CEMS 100K.

Table 2
Mossbauer parameters for oxides formed on the surface of weathering steel

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>α-FeOOH</th>
<th>γ-FeOOH</th>
<th>γ-Fe_{2}O_{3}</th>
<th>α-Fe_{2}O_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>300</td>
<td>100</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>IS (mms^{-1})</td>
<td>31</td>
<td>38</td>
<td>.34</td>
<td>.39</td>
</tr>
<tr>
<td>QS (mms^{-1})</td>
<td>.95</td>
<td>.95</td>
<td>.59</td>
<td>.60</td>
</tr>
<tr>
<td>H (kOe)</td>
<td>292,327</td>
<td>469,486</td>
<td>26</td>
<td>1.45</td>
</tr>
<tr>
<td>Linewidth (mms^{-1})</td>
<td>.42</td>
<td>.43</td>
<td>.26</td>
<td>.30</td>
</tr>
<tr>
<td>Area Fraction</td>
<td>24</td>
<td>10</td>
<td>8</td>
<td>44</td>
</tr>
<tr>
<td>PA</td>
<td>15</td>
<td>12</td>
<td>12</td>
<td>34</td>
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</table>

exposures to seawater and the initial corrosion products are γ-FeOOH and ferrhydrite which form semi-cohesive films on the surface. A small amount of α-FeOOH is also present and is probably formed from conversion of the γ-FeOOH. No dehydrated oxides, γ-Fe_{2}O_{3} or α-Fe_{2}O_{3} were formed after the short exposure. A similar observation was made with the weathering steels even though the nature of the oxides present were more varied. The predominant oxide α-FeOOH is found below the crusty protective layer of amorphous hydroxyoxide which was not well characterized in the present studies. More α-FeOOH in the Saylorsburg sample indicates that in a dryer atmosphere, the conversion from γ-FeOOH is more readily achieved. Very little of the dehydrated oxides were found but it is expected that after longer exposures, some of the crusty layer will be converted to γ-Fe_{2}O_{3} or α-Fe_{2}O_{3}.

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References
/1/ D.C. Cook and E. Agyekum, Nucl. Instr. Meth. (accepted for publication)